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FREDERICK G. COTTRELL, DIRECTOR

DETERMINATION OF MOLYBDENUM

BY

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This Report is the Result of Work Done Under Cooperative Agreements with the College of Mines, University of Washington, and the Colorado School of Mines

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DETERMINATION OF MOLYBDENUM.

J. P. Bonardi and Edward P. Barrett.

INTRODUCTION.

This report presents the results of an investigation by the Bureau of Mines on methods of determining molybdenum. It points out certain disadvantages in the methods hitherto used when applied to low-grade ores, and describes improved methods of both volumetric and gravimetric analysis, perfected in the bureau's laboratories, that are more rapid and accurate than any previously devised. Also, comparison is made of the two methods, as regards their application and relative advantages.

SCOPE OF REPORT.

During the recent activity in the molybdenum market the old and well-known methods for the determination of molybdenum in ores were found inadequate. They were satisfactory for small tonnages of high-grade material, but, on account of the advent of flotation methods and the inflation of the market because of the war, the tonnage became so large and the grade of products so low that the percentage of molybdenum needed to be determined to the second decimal place.

The failure of analytical methods of determination to keep pace with the magnitude of operations became evident when a tailing sample, from a flotation experiment, which contained 0.13 per cent molybdenum, was submitted for analysis to a reliable commercial laboratory. The laboratory reported a "trace" of molybdenum. The company that submitted the sample was milling 200 tons of ore a day; therefore, if the value of molybdenum at the mill is placed at 75 cents a pound, the 0.13 per cent in the tailing represents a loss or a gain of about $400 a day. This incident happened during the war, when the Bureau of Mines was making an effort to stimulate the production of molybdenum and at the same time to reduce losses. The bureau, therefore, began an investigation to devise a more accurate method for determining molybdenum in low-grade ores.

The results of the first efforts disclosed the fact that the required degree of accuracy was difficult to obtain by the various methods in use. The method used must be rapid as well as accurate, as a company treating a low-grade ore must know the results not later than the day after the samples are taken in order to control closely the mill and the mine.

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This report presents data and notes collected in the study of the causes for discrepancies and errors found in many methods when used for the determination of molybdenum in low-grade materials. The gravimetric method described was worked on by E. P. Barrett at the Seattle station of the Bureau of Mines, and the volumetric method by J. P. Bonardi at the Bureau of Mines station at Golden, Colo. The preliminary work was done independently, and when the methods had been somewhat mastered, Mr. Bonardi was detailed to Seattle temporarily and results from both methods were compared. Further new data was collected for both methods, and all the necessary factors were determined and definitely established by several series of analyses of low-grade ores.

ACKNOWLEDGMENTS.

The writers express their appreciation of the assistance of F. K. Ovitz, superintendent of the Seattle station, and R. B. Moore, superintendent, and S. C. Lind, acting superintendent, of the Golden station of the Bureau of Mines, who made it possible for them to work together in the preparation of this report. Credit is due W. H. Coghill, metallurgist of the Seattle station, for suggesting the importance of the work, which he had occasion to bring out in connection with his study of flotation methods for molybdenite. The authors are also indebted to these gentlemen for advice and suggestions offered in the preparation of the report.

QUALITATIVE TESTS.

In the analysis of low-grade molybdenum ores, qualitative tests for molybdenum in residues and products are often necessary.

One of the most highly recommended tests is to fuse some of the pulverized ore with sodium or potassium carbonate to which a small amount of potassium nitrate has been added. The fusion is leached with water, heated, and filtered; the filtrate is acidified with hydrochloric acid and boiled several minutes to expel all carbon dioxide. Some ammonium or potassium thiocyanate and a piece of metallic zinc are added; if molybdenum is present a bright cherry-red color rapidly develops that will disappear on standing in the presence of zinc, the time the color remains depending upon the proportion of molybdenum present. If hydrogen peroxide is added to the solution immediately after the cherry-red color has developed, the color disappears, but returns as soon as the peroxide has been reduced. When only a small proportion of molybdenum is present, if the solution is shaken with a small volume of ether immediately after the thiocyanate and zinc have been added, any color in the liquid will be extracted by the ether and intensified as a golden brown in the ether ring that forms at the top of the liquid on standing. This makes visible color that before may have been imperceptible.[a]

[a] Prescott, A. B., and Johnson, O. C., Qualitative chemical analysis, 5th ed., 1903, p. 96.

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Should the fusion be imperfect and an extraction of iron be present in the leach from the fused carbonates, a cherry-red color will immediately develop on the addition of the potassium or ammonium thiocyanate to the solution. On adding zinc, however, the color due to iron disappears, and, unless a large quantity of iron has been brought into solution, this color will completely disappear prior to the development of any color due to molybdenum. If this color reaction of iron and its disappearance on addition of zinc is borne in mind, the above test for molybdenum is infallible.[a]

A standard test for alkaline solutions of molybdates is the addition of tannic acid.[b] If molybdenum is present the solution will be colored deep red to brown.

Another test, which is a modification of that given by Scott,[c] is to place a pinch of powdered ore on a porcelain lid, moisten with a few drops of nitric acid so as to make a paste, heat nearly to dryness, then add 0.5 c. c. of concentrated sulphuric acid, heat to fumes and let stand. If molybdenum is present, breathing on the ore will produce a blue color; a drop of alcohol added at this point will hasten the color reaction. The color will disappear on heating, but the ore is again permitted to stand for some time, will reappear on cooling. Water will also destroy the color.

An alkaline solution of a molybdate free from iron, after acidifying with acetic acid, will, on the addition of potassium ferrocyanide or tannic acid, become deep red to brown. Pyrogallol, under similar conditions, will give an orange color. Molybdenum present as ammonium molybdate in a nitric-acid solution is precipitated by microcosmic salt ($NaNH_4HPO_4 4H_2O$) as yellow ammonium phosphomolybdate. The precipitate is soluble in sodium or ammonium hydroxide.

REVIEW OF QUANTITATIVE METHODS IN GENERAL USE.

Some of the methods for the determination of molybdenum that are in general use are as follows: (1) Precipitation as the sulphide from acid or alkaline solutions with or without increased pressure; (2) precipitation as mercurous molybdate; (3) precipitation as lead molybdate; (4) titration with lead acetate; (5) titration with potassium permanganate; (6) titration with titanium chloride; (7) the iodometric method; and (8) titration with potassium iodate. These methods are briefly as follows:

PRECIPITATION AS THE SULPHIDE.

The precipitation of molybdenum as the sulphide from acid or alkaline solutions, with or without increased pressure, requires either that the precipitated sulphides be converted to some weighable form

[a] Horton, F. W., Molybdenum: its ores and their concentration: Bull. 111, Bureau of Mines, 1916, p. 40.

[b] Prescott, A. B., and Johnson, O. C., work cited, 5th ed., 1903, p. 97. Moir, James, Qualitative tests for molybdenum: Jour. Chem. Met. Min. Soc. South Africa, vol. 16, 1916, pp. 191-2.

[c] See Scott, W. W., Standard methods of chemical analysis, 2d ed., 1917, p. 275.

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such as MoO_3 or MoS_2, or that the sulphides be dissolved, passed through a Jones reductor, and titrated with potassium permanganate. The conversion of MoS_3 to MoO_3 is a long and tedious process. MoO_3 is volatile at a temperature of about 400° to 450° C. and complete conversion to MoO_3 requires long ignition at a temperature of about 350° C. Binder [a] states: Molybdenum precipitated as MoS_3 and ignited to MoO_3 is not completely oxidized unless treated with HNO_3, evaporated, dissolved in NH_4OH, reprecipitated with HNO_3, evaporated, and ignited. A correction must be made for any trace of matter which remains insoluble when the ignited residue is dissolved in NH_4OH.

In reducing MoS_3 to MoS_2 in a stream of hydrogen in a Rose crucible, many ignitions and weighings are sometimes necessary to obtain constant weights. These processes require considerable care and practice.

PRECIPITATION AS MERCUROUS MOLYBDATE.

The precipitation as mercurous molybdate requires the same care as the preceding method. In addition, chromium, vanadium, tungsten, and phosphorus interfere with the determination.[b]

PRECIPITATION AS LEAD MOLYBDATE.

Regarding the precipitation as lead molybdate, Scott [c] says:—

This method, suggested by Chatard, has been pronounced by Brearly and Ibbotson to be one of the most stable processes found in analytical chemistry. It is not interfered with by the presence of large amounts of acetic acid, lead acetate, or alkali salts (except sulphates). The paper need not be ignited separately and prolonged ignition at a much higher temperature than necessary to destroy the paper does no harm. From faintly acid solutions lead molybdate may be precipitated free from impurities in the presence of copper, cobalt, nickel, zinc, manganese, magnesium, and mercury salts. It may be readily separated from iron and chromium. Barium strontium, uranium, arsenic, cadmium, and aluminum do not interfere if an excess of hydrochloric acid has been added to the solution followed by lead acetate and sufficient ammonium acetate to destroy the free mineral acid. The precipitate is granular, easily filtered and washed. Vanadium and tungsten interfere, but may be readily separated from the molybdenum.

Rather[d] also refers to this method.

TITRATION WITH LEAD ACETATE.

Titration with lead acetate is the reverse of the ammonium molybdate method for the determination of lead and has the same limitations. The color change of the tannic acid solution is not sharp enough for use on low-grade materials.

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[a] Binder, O., [Estimation of molybdenum]: Chem. Ztg., Jahrg. 42, 1918, p. 225. Abstract in Chem. Abs., vol. 12, 1918, p. 2174.

[b] Scott, W. W., Standard methods of chemical analysis, 2d ed., 1917, p. 279.

[c] Scott, W. W., work cited, p. 278.

[d] Rather, J. B., Molybdic acid: Jour. Assoc. Official Agr. Chem., vol. 1, 1915, pp. 317-29; vol. 2, 1916, p. 39.

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TITRATION WITH POTASSIUM PERMANGANATE.

Titration with potassium permanganate comprises reducing the molybdenum solution in a Jones reductor and titrating with potassium permanganate. This is a stable process and gives accurate results. The variables are easily controlled, and the method can be used for assaying high-grade as well as low-grade material.

TITRATION WITH TITANIUM CHLORIDE.

Titration with titanium chloride applies more generally to the determination of molybdenum in steel.[a]

IODOMETRIC METHOD.

By the iodometric method a mixture of molybdic acid and potassium iodide is boiled in the presence of hydrochloric acid, the volume having defined limits. Free iodine is liberated and expelled, and the molybdic acid is reduced to a definite lower oxide.[b] The reaction is as follows:

$$2MoO_3+4KI+4HCl=2MoO_2I+I_2+4KCl+2H_2O.$$

This method finds no practical application, because of the difficulty of obtaining a quantitative reduction in accordance with the above equation.[c]

TITRATION WITH POTASSIUM IODATE.

In titration with potassium iodate an acid solution of the molybdenum is passed through a Jones reductor, the solution is received in a flask containing a solution of ICl in the presence of HCl, and the molybdenum is titrated with a solution of KIO_3. The reaction[d] is as follows:

$$Mo_2O_3+KIO_3+2HCl=Mo_2O_5+ICl+KCl+H_2O.$$

COMMENTS ON ADAPTABILITY TO LOW-GRADE ORES.

The foregoing methods were carefully studied to determine their adaptability to the determination of molybdenum in low-grade material, the length of time necessary to complete the determination always being considered. The following comments refer to the methods in the order given:

The precipitation as sulphides was not tried out, because the method was considered too tedious and the amount of precipitated

[a] Travers, M., Nouveau dosage volumétrique du molybdène et du vanadium dans les aciers, Compt. rend., t. 165, 1917, p. 362; abstract in Eng. and Min. Jour. vol. 106, 1918, p. 585; and Jour. Soc. Chem. Ind. Oct. 31, 1917.

[b] Gooch, F. A., and Fairbanks, Charlotte, The iodometric estimation of molybdic acid: Am. Jour. Sci. ser. 4, vol. 2, 1896, p. 160. Gooch, F. A., and Pullman, O. S., jr., The estimation of molybdic acid reduced by hydriodic acid: Am. Jour. Sci., ser. 4, vol. 12, 1901, p. 449.

[c] Treadwell, F. P., and Hall, W. T., Analytical chemistry, vol. 2, 3d ed., 1912, pp. 666–67.

[d] Jamison, G. S., On the determination of molybdenum by potassium iodate: Jour. Am. Chem. Soc., vol. 39, 1917, pp. 246–9.

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sulphides too small, as precipitated MoS_3 contains only 0.50 per cent Mo. The conversion to some weighable form also offers too many difficulties.

The precipitation as mercurous molybdate was not tried, as it offered practically the same difficulties as the preceding method.

The precipitation as lead molybdate was tried out because it seemed to offer possibilities for accurate analysis of low-grade material, as the precipitate $PbMoO_4$ represents 26.15 per cent Mo. Furthermore, no special precautions are necessary in igniting the precipitate.

The titration with lead acetate was tried only on low-grade material assaying less than 0.15 per cent molybdenum. The method was unsatisfactory, as the insoluble lead molybdate did not form a precipitate immediately and the end point with tannic acid was not dependable.

Many experiments were made with the method of reduction of the molybdenum and titration with potassium permanganate. This method is accurate, rapid, and adaptable to use with all the ores of molybdenum, regardless of the method of decomposition. However, it has certain well-defined variables that must be absolutely understood and controlled.

The other methods were not tried out, as the gravimetric ($PbMoO_4$) and the volumetric ($KMnO_4$) methods gave satisfactory results.

METHODS OF DECOMPOSITION.

Methods of decomposition that have been suggested are as follows:

Fusion with sodium peroxide;[a] fusion with sodium or potassium carbonates or mixtures of the carbonates, with a small amount of potassium nitrate present to oxidize the sulphides;[b] fusion with potassium bisulphate;[c] decomposition with aqua regia; decomposition with aqua regia followed by the addition of sulphuric acid and heating to fumes.[d]

Fusion methods offer rapid and complete decomposition of the ores.

Decomposition by aqua regia is applicable to ores carrying no lead.

Decomposition by aqua regia, followed by the addition of sulphuric acid and heating to fumes, is especially applicable to ores carrying lead. This is the method used for wulfenite ores.

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[a] Darroch, James, and Meiklejohn C. A.: A rapid method of determining molybdenum; Eng. and Min. Jour., vol. 82, 1906, p. 818.

[b] Horton, Frederick W., Molybdenum: Its ores and their concentration; Bull. 111, Bureau of Mines, 1916, p. 41.

[c] Mabee, H. C.: Molybdenum content of ores and concentrates; Eng. and Min. Jour., vol. 105, No. 18, 1918, p. 836.

[d] Colett, E., and Eckhardt, M.: Bemerkungen zur Bestimmung des Molybdans im Molybdänglanz; Chem. Ztg., Jahrg. 33, Bd. 96, 1909, p. 968.

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VOLUMETRIC (POTASSIUM PERMANGANATE) METHOD FOR LOW-GRADE ORE.

The ore is decomposed either by acid or by fusion with Na_2O_2 into a soluble molybdate and insoluble compounds of the other constituents of the ore. The molybdate is filtered, acid added, and the solution is passed through a Jones reductor where the MoO_3 is reduced to Mo_2O_3. The Mo_2O_3 is then titrated with $KMnO_4$, and the percentage of molybdenum present is calculated.

PROCEDURE FOR ACID DECOMPOSITION.

Weigh out 0.5 to 5 grams of ore, depending on its richness in molybdenum. The content of the portion taken for analysis should not exceed 0.08 gram Mo, as explained under "Size of Sample" (p. 14). Decompose the sample with aqua regia in an Erlenmeyer flask, heating for 15 minutes. Cool the solution, add 20 c. c. of dilute (1:1) sulphuric acid, evaporate to fumes, cool again, dilute, neutralize without filtering off the insoluble matter and add 10 c. c. excess of ammonium hydroxide, boil and filter, and wash with hot water five times. Redissolve the precipitate into the original Erlenmeyer flask by puncturing the filter paper, washing the content into the flask and dissolving with dilute sulphuric acid. Reprecipitate, boil, filter, and wash well. The filtrate should be clear and colorless; add enough dilute sulphuric acid so that there will be present after neutralizing all the ammonia, at least 12.5 c. c. of free concentrated sulphuric acid for each 250 c. c. of solution. The solution is now ready to be reduced by passing through the Jones reductor.

INTERFERING ELEMENTS.

This method of solution by digesting with aqua regia, adding sulphuric acid and evaporating to fumes, and then boiling with ammonia, brings all the molybdenum into solution. The residue rarely, if ever, contains molybdenum. Nitric acid used in place of aqua regia in combination with sulphuric acid taken to fumes will also give excellent results. Either of these two methods will completely dissolve the molybdenum in molybdenite and wulfenite ores, and also in ferromolybdenum if ground sufficiently fine. The silica, iron, alumina, lead, and other sulphates and insoluble matter will be found in the precipitate.

Copper and arsenic, if present, can be removed by adding several grams of zinc to the acid solution before passsing it through the reductor, where some of the arsenic is evolved as arsine. The copper when precipitated by the zinc will also precipitate the remaining arsenic. If much arsenic is present, the addition of a few c. c. of a 10 per cent solution of copper sulphate may be necessary. Antimony, if present, acts in a manner similar to arsenic.

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Procedures for the separation of molybdenum from tungsten and vanadium are given in standard works listed in the bibliography at the end of this paper. When vanadium is present in the ore—for example, wulfenite occurring with vanadinite, as it often does—the vanadium can be determined volumetrically by titration with the permanganate solution, as described by Scott.[a] Vanadium can also be determined by the rapid method of reduction with HCl, in which arsenic or molybdenum do not interfere. This method is described by Moore and Kithil.[b]

Molybdenum may be precipitated as the sulphide from slightly acid solutions by passing H_2S under pressure into the solution, as described fully in standard textbooks and in the references given in this paper. The addition of 2 grams of tartaric acid will prevent precipitation of vanadium and tungsten along with the molybdenum. The same procedure may be applied to ammoniacal solutions, but the solution must be made slightly acid before the molybdenum will precipitate as the sulphide. The molybdenum sulphide may then be redissolved in strong nitric acid, fuming with sulphuric acid as previously described. Any copper sulphide liable to precipitate with the molybdenum sulphide does not interfere with the volumetric method, but does with the gravimetric sulphide method of determination.

DECOMPOSITION BY FUSION WITH SODIUM PEROXIDE.

Decomposition by fusion with sodium peroxide is practically the same procedure for preparing the solution of molybdenum that is used by one of the largest producers and refiners of molybdenum ores and products in this country. This method has proved fairly accurate for determining molybdenum in low-grade materials, and a complete determination can be made in 30 minutes.

PROCEDURE.

Weigh out a 0.5 to 5 gram sample, according to the grade of the ore; the content of Mo should not exceed 0.15 gram, as explained under "Size of Sample" (p. 14). Place the weighed sample in a 60-c. c. iron-spun crucible and thoroughly mix with six times as much sodium peroxide. Cover the crucible with an iron lid, and heat in an electric muffle maintained at a temperature of about 600° C., or in the flame of a Meeker burner, until perfect fusion is obtained. Fusion takes place in about ten minutes in the muffle, and in about five minutes over the burner. Allow the crucible to cool for a few minutes; then while still warm place in an 800-c. c. beaker containing 400 c. c. of water. After solution, which takes

[a] Scott, W. W.: Standard methods of chemical analysis; 2d ed. rev., 1917 p. 282.

[b] Moore, R. B., and Kithil, K. L.: A preliminary report on uranium, radium, and vanadium; Bull. 70, Bureau of Mines, 1914, p. 90.

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place quickly, remove the crucible and the cover with iron tongs and wash them with water from a wash bottle. If excess silica is present, boil before making up to volume. Make up the volume in a graduated flask to 500 c. c. and filter the solution through four folded sheets of 8-inch filter paper placed in a 5-inch funnel.

A good grade of bleached paper should be used, because with unbleached paper the organic matter dissolved by the hot caustic solution will require several c. c. of permanganate solution for the blank titration. One grade of paper tested was so poor that as much as 10 c. c. of one-twentieth normal permanganate was required to color the filtrate permanently after it had been made acid. The quantity required for blanks in the peroxide fusion method should never exceed 0.8 c. c.

Filtration takes place quickly. When 250 c. c. have filtered through, stop filtering, add enough dilute (1:1) sulphuric acid to the filtrate so that after the caustic has been neutralized the solution will contain approximately 12.5 c. c. of free sulphuric acid. Heat the 250 c. c. of acidified solution on the hot plate for several minutes to drive off any hydrogen peroxide that may have formed. The acid solution is then ready to be passed through a Jones reductor.

INTERFERING ELEMENTS.

Fusion with sodium peroxide will completely and readily convert all the molybdenum into soluble sodium molybdate. When the fusion is dissolved in water the iron will be completely precipitated with other insoluble hydroxides, including copper. With low-grade material the amount of molybdenum retained by the bulky precipitate is of no consequence in the calculations. However, with high-grade material, the precipitate should be redissolved and again precipitated, as only an aliquot part of the filtrate is taken for analysis and the amount of molybdenum retained by the precipitate may materially affect the results. Other interfering elements that may occur in the leached molybdenum solution may be removed or determined as in acid decomposition (p. 9).

If the alkaline leached solution obtained by fusing an ore rich in silica is neutralized with dilute acid and an insufficient excess, only a few c. c., of acid is present, colloidal silicic acid will be precipitated when the solution is heated. On titrating the solution after it has been passed through the reductor, low results will be obtained, and the end point will fade quickly and be uncertain. (See p. 17.) The concentration of acid used, 12.5 c. c. in 250 c. c. volume, prevents this precipitation if the solution is not boiled too long. If too much silicic acid separates, the better plan is to take a new sample rather than attempt to run the gelatinized solution through the reductor.

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JONES REDUCTOR.

The Jones reductor is illustrated and described by Lord and Demorest,[a] also by Scott.[b] It consists of a glass tube which is contracted at the bottom, with a 3-inch funnel inserted at the top. The internal bore and length of tube are important considerations. The stem of the funnel enters a small one-hole rubber stopper, which fits tightly into the top of the glass tube. The stem, or contracted end of the tube enters the rubber stopper of a 2-liter side-neck flask that is connected by pressure tubing to a suction pump.

The zinc for the reductor should be of 20-mesh size and contain less than 0.01 per cent iron. It is best amalgamated as follows: With very dilute H_2SO_4—about 3 c. c. to 100 c. c. of water—moisten in a beaker a sufficient quantity of zinc to fill the reductor, add a small drop of mercury, and stir until uniformly white. Wash the zinc free from acid and put it into the tube. One-half gram of mercury is sufficient for 150 grams of zinc. Avoid using more than just enough.

The reductor is filled by placing some glass beads at the neck; on the beads is placed some glass wool mixed with bits of small broken glass rods to prevent the wool from forming a compact plug that might hinder the passage of the solution. Above the wool may be placed a perforated platinum disk or gauze, to assist the clear passage of the solution and to prevent clogging. The tube is then filled to within a few inches of the top with the amalgamated zinc.

The internal bore of the reductor should not be greater than five-eighths of an inch. The reductor should be 20 to 30 inches long. Shorter reductors, ranging down to 10 inches, and larger bores than five-eighths of an inch were tried, but the results were unsatisfactory, owing to the following reasons:

(*a*) The molybdenum solution was not completely reduced by passing the liquid through once, which necessitated passing the solution through a second time and required a larger blank correction. This factor must be carefully controlled, as shown later.

(*b*) The quantity of solution or wash water necessary to wash a reductor completely when using one of larger bore than five-eighths of an inch makes the solution too bulky to titrate. In order to obtain a sharp end point the solution must not be too dilute. The titrations obtained on blank runs, with the same quantity of acid and solution as in a molybdenum determination for several reductors of different construction, varied from 0.5 to 1.5 c.c., and, in one test, as high as 2 c. c., of 1/20 normal permanganate. The largest blank was later proved to be due to overamalgamation of the zinc, as the reductor had been used for several hundred determinations and much of the zinc had been dissolved.

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[a] Lord, N. W., and Demorest, D. J., Metallurgical analysis, 1916, pp. 29–30.
[b] Scott, W. W., Standard methods of chemical analysis, 2d ed., 1917, p. 281.

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METHOD OF USING REDUCTOR.

A stock solution of acid wash water should be made up containing about 50 c. c. of concentrated sulphuric acid per liter. One hundred c. c. of acid wash is passed through the reductor at a temperature of 60° to 70° C., or as hot as can be conveniently handled. This heats the zinc, making the reduction more effective, and removes air from the apparatus. Then the molybdenum solution, heated to the same temperature, is passed through, followed by 200 c. c. more of hot acid wash, and 200 to 250 c. c. of hot water. The reduced solution should be immediately titrated.

The rate of flow should not be greater than 50 c. c. in 30 seconds, and can be accurately controlled by the suction pump. A faster rate may give erratic results, especially with high-grade material.

Care should be taken that no air is drawn through the zinc. If this happens and the air is immediately followed by dilute acid, the liquid running through is sometimes oxidized, possibly from the formation of H_2O_2; hence, while the solution and the wash water are being run through the reductor, the surface of the zinc must be kept covered continually with liquid.[a] The funnel on the reductor should not be permitted to drain before the run is finished.

Complete reduction is denoted by the green color imparted to the solution when the molybdenum has been reduced from MoO_3 to Mo_2O_3. In analyzing low-grade material under the given conditions, the use of ferric phosphate solution in the receiving flask of the reductor is not essential, although it is with high-grade ore.

Only enough wash liquid to remove the molybdenum completely should be used. Too much washing increases the blank and makes the titrating solution too large for a sharp end point. After several runs the quantity of wash liquid stated—that is, 200 c. c. of hot acid wash followed by 200 to 250 c. c. of hot water—was found to wash the molybdenum completely from a reductor ranging from 20 to 30 inches in length and to give a blank determination of 0.35 c. c. to 0.50 c. c. of one-twentieth normal permanganate solution. This result was as good as could be obtained. Fifty c. c. of concentrated sulphuric acid to one liter of water proved to be the best concentration of acid wash. Greater concentration of acid, however, is not detrimental. The concentration of acid in 250 c. c. of the molybdenum solution should, as previously stated, be 12.5 c. c.

As 1 c. c. of one-twentieth normal permanganate solution is equivalent to 0.0016 gram molybdenum, or 0.16 per cent molybdenum on a 1-gram sample, too much care can not be taken in the use of the reductor.

[a] Gooch, F. A., Methods of chemical analysis, 1912, p. 430.

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TITRATION.

The determination of the molybdenum in solution will be accurate and dependable only when the following directions for volumetric titration with permanganate are carefully carried out. The sample of the reduced molybdenum solution that is to be titrated should not be too large, nor the permanganate solution too strong, and before the molybdenum solution is titrated a blank determination should be made exactly as in the molybdenum determination.

SIZE OF SAMPLE.

Five grams should be taken of any ore supposed to assay less than 3 per cent Mo, 1 gram of an ore assaying in the vicinity of 15 per cent Mo, and one-half gram for ore assaying above 15 per cent; a proper aliquot part of the solution should be used when titrating with a weak permanganate solution. The reason for controlling the size of sample used is evident. When titrating an aliquot part—for example one-half the weight of the sample taken, as in the method of fusion with sodium peroxide—the reading for one-twentieth normal potassium permanganate should fall on the scale of a 50-c. c. burette.

NORMALITY OF POTASSIUM PERMANGANATE.

A potassium permanganate solution of approximately one-twentieth normal strength was selected for low-grade material because 1 c. c. of such a solution represents 0.0016 gram Mo, or 0.16 per cent on a 1-gram basis. A 5-gram sample of ore containing 0.16 per cent Mo. would then require only 5 c. c. of the permanganate solution. As the molybdenum content to be determined in low-grade material usually falls below 0.10 per cent, the use of stronger solutions is not advisable because the volume required for titration would be too small for accurate control.

An attempt was made to use a weaker permanganate solution, of 1/100 normal strength, where 1 c. c. would represent 0.00032 gram Mo, or 0.032 per cent on the 1-gram basis, but the end point of such a weak solution was uncertain and could not be controlled within 1 c. c. and often not within several c. c. Also a blank determination required several c. c., an unreliable quantity. With very high-grade material the use of a solution stronger than 1/20 normal may be necessary in order that a larger sample may be taken for analysis.

EFFECT OF BLANK.

When the amount of permanganate required for a blank run is being determined, the acid concentration of the solution, the volume of wash water used, and the manipulation of the reductor should be the same as in the molybdenum determination. One large chemical

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concern that buys and sells molybdenum ore has not been subtracting a correction factor for ore assaying more than 5 per cent molybdenum, but does subtract the correction for molybdenum content below 5 per cent. The following experiments were made in order to determine the effect of the blank in titrating reduced molybdenum solutions of different strengths. The blank requirement for the reductor used in these experiments was 0.35 c. c. of 1/20 normal permanganate.

Two grams of approximately 100 per cent MoO_3 were dissolved in ammonia and the solution made up to 50 c. c. Aliquot portions were drawn off with five different-sized pipettes so that the quantity of molybdenum would correspond to the content found in various grades of ores. The molybdenum in each pipette was carefully determined by the gravimetric method, weighing as lead molybdate, and by titration. Each volumetric determination was made in duplicate or triplicate, so that the limit of accuracy with this method could also be determined. The results were as follows:

Results of first set of experiments.

1. 50 c. c. of solution=0.1327 gram Mo by gravimetric ($PbMoO_4$) method.
   50 c. c. of solution=82.60 c. c.
   50 c. c. of solution=82.80 c. c. } $\frac{1}{20}$ normal permanganate, volumetric method.
   50 c. c. of solution=82.80 c. c.
   Average number of c. c. required=82.73=0.1324 gram Mo.
   Difference from gravimetric=−0.0003 gram Mo.
   No blank subtraction necessary.
2. 25 c. c. of solution=0.0664 gram Mo by gravimetric ($PbMoO_4$) method.
   25 c. c. of solution=41.20 c. c.
   25 c. c. of solution=41.40 c. c. } $\frac{1}{20}$ normal permanganate, volumetric method.
   Average number of c. c. required=41.30=0.0661 gram Mo.
   Difference from gravimetric=−0.0003 gram Mo.
   No blank subtraction necessary.
3. 10 c. c. of solution=0.0264 gram Mo by gravimetric ($PbMoO_4$) method.
   10 c. c. of solution=16.90 c. c.
   10 c. c. of solution=16.90 c. c. } $\frac{1}{20}$ normal permanganate, volumetric method.
   Average number of c. c.=16.90=0.02705 gram Mo.
   16.90−0.35 c. c. (blank subtraction)=16.55 c. c.=0.0264 gram Mo.
   Blank subtraction required.
4. 5 c. c. of solution=0.0128 gram Mo by gravimetric ($PbMoO_4$) method.
   5 c. c. of solution=8.40 c. c.
   5 c. c. of solution=8.60 c. c. } $\frac{1}{20}$ normal permanganate, volumetric method.
   Average number of c. c.=8.50=0.01360 gram Mo.
   8.50−0.35 c. c. (blank subtraction)=8.15=0.0130 gram Mo.
   Difference from gravimetric=+0.0002 gram Mo.
   Blank subtraction required.
5. 1 c. c. of solution=0.002484 gram Mo by gravimetric ($PbMoO_4$) method.
   1 c. c. of solution=1.80 c. c.
   1 c. c. of solution=1.90 c. c. } $\frac{1}{20}$ normal permanganate, volumetric method.
   Average number of c. c.=1.85=0.002960 gram Mo.
   1.85 c. c.−0.35 c. c. (blank subtraction)=1.50 c. c.=0.00240 gram Mo.
   Difference from gravimetric=−0.00008 gram Mo.
   Blank subtraction required.

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The results were so significant that the experiment was repeated. A different molybdate solution that had been standardized against pure lead was used, and the molybdenum solution was titrated against lead acetate. In 1 liter of water 4.74 grams of $(NH_4)_6Mo_7O_{24}.4H_2O$ was dissolved and standardized against 0.20 gram of pure lead foil, as given by Low[a], in the determination of lead, using a standard molybdate solution.

Results of standardization.

10 c. c. of the molybdate solution=0.0054 gram Pb=0.02502 gram Mo.
By gravimetric ($PbMoO_4$) method, 10 c. c. of solution=0.02472 gram Mo.
Difference=0.0003 gram Mo.
Average for 10 c. c.=0.02487 gram Mo.

Results of second set of experiments.

1 c. c. of molybdate solution requires 1.90 c. c. of permanganate−0.35 c. c. (blank) =1.55 c. c.=0.002480 gram Mo.
5 c. c. of molybdate solution requires 7.80 c. c. of permanganate−0.35 c. c. (blank) =7.45 c. c.=0.01202 gram Mo.
10 c. c. of molybdate solution requires 15.90 c. c. of permanganate−0.35 c. c. (blank) =15.55 c. c.=0.02488 gram Mo.
25 c. c. of molybdate solution requires 38.60 c. c. of permanganate (no blank subtraction)=38.60 c. c.=0.06176 gram Mo.

Difference on 1 c. c.	−0.000007 gram Mo.
Difference on 5 c. c.	−0.0004 gram Mo.
Difference on 10 c. c.	+0.0001 gram Mo.
Difference on 25 c. c.	−0.0004 gram Mo.

These results indicate that no blank should be subtracted on a molybdenum solution that requires more than 16 c. c. of a one-twentieth normal permanganate solution; this quantity corresponds to 0.0256 gram Mo and, on the basis of an 0.5-gram sample, is equivalent to 5.12 per cent Mo. For a permanganate consumption below 16 c. c. a blank should be subtracted. The reason for this conclusion is more evident when one considers the following facts regarding the use of such a weak solution as one-twentieth normal permanganate.

Pure distilled water containing the same acid concentration as used in a determination will usually require 0.20 c. c. of one-twentieth normal permanganate to effect a color in 250 c. c.; also, when a blank is run through a reductor, if any H_2O_2 is formed and oxidization takes place in the liquid, some permanganate may be consumed. When a weak solution of molybdenum is run through the reductor, possibly the weak effect of any oxidizing substance due to the presence of a trace of H_2O_2 does not act upon the reduced molybdenum; but when a strong solution is run through the reductor an oxidizing effect may act upon the reduced molybdenum, and thus compensate for the blank subtraction.

[a] Low, A. H., Technical methods of ore analysis, 1913, p. 151

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Whether the above explanation is the true one or not, the fact remains that when titrating a strong molybdenum solution no blank need be subtracted. Although the correction may be important when a solution representing an 0.5-gram sample is titrated, the blank effect is small if the solution represents 2.5 grams or more. The small blank, 0.35 c. c. or 0.50 c. c., would then be divided by 2.5 or more in calculating to a 1-gram basis to obtain the true percentage, and a fraction of one-tenth c. c. represents a negligible amount of molybdenum.

PRECAUTION AGAINST FADING END POINT.

In titrating the molybdenum solution obtained from an ore high in silica that had been fused, the end point vanished. This result may have been due to the presence of silica and other salts in the solution, which perhaps retarded the reaction, because fading did not occur when pure MoO_3 or ammonium molybdate, or the solution prepared by the acid-digestion method, was titrated. In order to overcome this difficulty a titrating mixture was made as follows: 100 grams of pure ammonium ferric sulphate

$$[(NH_4)_2SO_4.Fe2\ (SO_4)_3.24H_2O]$$

was dissolved in one liter of pure water; this was mixed with one liter of solution containing 90 grams of manganese sulphate, 175 c. c. of sirup of hypophosphate (H_3PO_4), and 175 c. c. of concentrated sulphuric acid. The phosphoric acid renders the solution colorless. Fifty c. c. of this mixture would be equivalent to approximately 0.275 gram Fe, or 0.1584 gram Mo, and would be sufficient for an ordinary molybdenum determination. The use of this solution in the receiver of the reductor tended to give a sharper end point, as is true when a reduced iron solution is titrated in the presence of a titrating mixture. On the other hand, a larger blank subtraction was necessary in each run. This applied to small or large amounts of molybdenum in solution and may have been partly due to some ferrous iron being present in the titrating mixture, or to other causes as given under "Effect of Blank" (p. 14). The indications are that a blank obtained without using a titrating mixture in the receiver is due mostly to causes other than dissolved ferrous iron. The following explanation will make this statement clearer.

Fifty c. c. of titrating mixture in 250 c. c. of water required 0.50 c. c. of one-twentieth normal permanganate, whereas 50 c. c. of titrating mixture in the Jones receiver, followed by a blank run, required 0.80 c. c. of the permanganate. Twenty-five c. c. of a molybdenum solution, as was shown under "Effect of Blank" required 41.30 c. c. of permanganate solution, whereas when the titrating mixture was used the permanganate reading was 42 c. c. Therefore, a blank must be subtracted when a titrating mixture is used in the

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receiving flask. One c. c. of molybdenum solution required 1.85 c. c. of permanganate without the mixture and 2.60 c. c. with the mixture in the receiver. Thus the use of this solution in the receiver was of no special advantage with the strengths of solutions titrated, although many analysts claim that its use is absolutely necessary to prevent the reduced molybdenum from being oxidized and to give a sharper end point. Reduction or oxidation gave no trouble in titrating solutions from low-grade ores of not more than 10 per cent molybdenum content, when the extra length of reductor was used as directed.

The end point, however, can easily be checked by passing the solution through the reductor a second time, which should give the same result as passing the solution through once. The bright green color indicates a complete reduction. The molybdenum solution should be titrated immediately; if it is allowed to stand, ferric phosphate solution should be used in the receiver, as recommended by Randall.[a] This point is also discussed in several standard text books.[b]

PRECAUTIONS FOR HIGH-GRADE ORE.

In working with higher grade material, carrying more than 10 per cent molybdenum, use of the ferric phosphate solution is recommended, as this would prevent reoxidation of a strong reduced molybdenum solution on exposure to the air, and would also give consistent results for any low-grade material analyzed. For experienced chemists, this precaution is not absolutely necessary, but its observance would perhaps be advisable for beginners.

A great deal has been written and many discussions have taken place concerning the state of reduction of the molybdenum after passing through the reductor. This controversy has been taken up in detail by Randall[c] and the reduction of the molybdenum to Mo_2O_3 has been proved conclusively.

If the volumetric method is used for assaying ores containing more than 50 per cent MoS_2, a large sample should be digested and an aliquot portion should be taken, besides a stronger solution of potassium permanganate than 1/20 normal should be used. However, the error even in such a determination must be multiplied by the factor for the aliquot portion taken that corresponds to a 1-gram sample in order to calculate the true percentage. With the gravimetric method, the chances of error in working with aliquot parts are small for high-grade material as a larger sample could be taken for analysis than in the volumetric method. A further advantage of

[a] Randall, D. L., The behavior of molybdic acid in the zinc reductor; Am. Jour. Sci., ser. 4, vol. 24, 1907, p. 313.

[b] Gooch, F. A., Methods of chemical analysis, 1912, p. 424. Scott, W. W., Standard methods of chemical analysis, 2d ed. rev., 1917, p. 281.

[c] Randall, D. L., Work cited, p. 313.

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the gravimetric method is the small factor (0.2615) that is used in multiplying the weight of lead molybdate to obtain the weight of molybdenum.

PRECAUTIONS WITH FERROMOLYBDENUM.

The sodium peroxide fusion method can be used in the determination of ferromolybdenum with the special precaution that after filtration the precipitated hydroxides must be redissolved, reprecipitated, and thoroughly washed. Ferric phosphate solution should be used in the receiving flask of the reductor to guard against oxidation of the strong reduced molybdenum solution.

LIMIT OF ACCURACY.

In the check determination for the volumetric method in the analyses given, and in many other analyses that were made, a difference of 0.20 c. c. for duplicates on the same sample was not uncommon. This difference, when calculated against 1/20 normal permanganate, represents 0.032 per cent Mo, or a weight of 0.00032 gram, on the basis of a 1-gram sample. This percentage would, no doubt, be about the limit of accuracy in comparing checks for molybdenum that was determined as the sulphide and ignited to MoO_3 and weighed. In the ignition method the separation of the sulphide from all other elements, especially copper, and the necessary accurate ignition to MoO_3 is unsatisfactory and uncertain, and must be attended with much precaution, particularly with low-grade material. This point is discussed in detail under the procedure for the gravimetric method. The difference between the molybdenum determined gravimetrically as lead molybdate and the molybdenum determined volumetrically by lead acetate titration, with tannic acid as an outside indicator, was 0.0003 gram, which for a 1-gram sample would represent 0.03 per cent; however, if the solution titrated represents a large sample, 2 to 5 grams, the limit of accuracy is 0.01 per cent or less, is the same as in the permanganate titration.

SUMMARY AND CONCLUSIONS AS TO VOLUMETRIC METHOD.

1. Decomposition with sodium peroxide is for low-grade ores the most rapid and reliable fusion method for obtaining molybdenum in solution.

2. The Jones reductor must be prepared and used according to the directions given herein in order to obtain accurate results.

3. The size of sample desirable for analysis and the strength of potassium permanganate used in titration depends on the grade of ore tested.

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4. A correction factor should applied to the titration result in order to counteract the "blank effect."

5. The limit of accuracy for the method is within 0.01 per cent on the basis of a 1-gram sample, if attended by the proper procedure.

6. Interfering elements found in molybdenum ores can be removed or determined.

7. The molybdenum in high-grade ores and in ferromolybdenum can be determined by this method if the proper precautions are taken

GRAVIMETRIC DETERMINATION OF MOLYBDENUM BY PRECIPITATING AND WEIGHING AS LEAD MOLYBDATE.

The following procedure has proved to be rapid and accurate for the analysis of low-grade materials. The method is fundamentally that outlined by Scott[a], in which he quotes the method of Chatard[b], but special attention is called to the details.

The ore is decomposed with acids and treated with ammonium hydroxide to form ammonium molybdate. From the hot solution the molybdenum is precipitated as $PbMoO_4$ by adding lead acetate solution in 2 or 3 c. c. excess, heating the mixture a few minutes, and filtering. The precipitated lead molybdate is then ignited, cooled, weighed, and the weight of molybdenum is calculated.

PROCEDURE FOR ACID DECOMPOSITION.

Weigh 0.25 to 5 grams of the finely pulverized ore into a 250 c. c. Erlenmeyer flask. Add 15 c. c. of nitric acid and heat until the brown fumes are gone. This is the most rapid manner of decomposing the sulphides present. Carefully add 5 to 10 c. .c of hydrochloric acid and heat about 20 minutes or until the ore is completely decomposed. Then evaporate to dryness, moisten with hydrochloric acid and wash down the sides of the flask with hot water and heat about 5 minutes longer. Cool the mixture, add 5 to 10 c. c. excess of ammonium hydroxide, heat a few minutes, and filter hot, washing with hot water at least 5 times. Puncture the filter paper and wash the residue of insoluble material (iron and aluminum hydroxides) into the Erlenmeyer flask, add sufficient hydrochloric acid to dissolve the precipitated hydroxides, make the solution slightly ammoniacal, heat, and filter into the same beakers that were used for the first filtration. Wash well with hot water. This second treatment is made in order to prevent an appreciable amount of molybdenum from being held mechanically in the residue.

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[a] Scott, W. W., Standard methods of chemical analysis; 2d ed., rev., 1918, p. 278.

[b] Chatard, T. M., On the determination of molybdic acid as plumbic molybdate: Am. Jour. Sci., ser. 3, vol. 1, 1871, p. 416.

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THE REMOVAL OF LEAD.

If the ore carries lead, as wulfenite, decompose with nitric acid and hydrochloric acid as previously stated, but after cooling add 10 c. c. of sulphuric acid and evaporate to dense fumes. Cool, add about 50 to 60 c. c. of water and heat to dissolve the soluble sulphates. Cool, filter to remove the insoluble material and lead, wash well, and add to the filtrate 5 to 10 c. c. excess of ammonium hydroxide; heat and filter. Repeat this precipitation in order to extract all the molybdenum from the residue.

THE REMOVAL OF PHOSPHORUS.

Phosphorus, when present, should be removed by the addition of a few c. c. of magnesia mixture to the ammoniacal solution before filtering off the iron and aluminum hydroxides. The ammoniacal solution should be warmed about 20 minutes to allow the precipitated magnesium phosphate to settle. If not removed, the phosphorus will precipitate as lead phosphate with the lead molybdate.

FURTHER PREPARATION OF THE SOLUTION.

The molybdenum is now in the form of ammonium molybdate in a solution practically free from silica, iron, and alumina, also lead if the sample was evaporated to fumes with sulphuric acid.

The volume of the solution should approximate 250 c. c. Acidify the solution with hydrochloric acid, using methyl orange as an indicator and adding about 5 c. c. excess acid. The use of hydrochloric acid in neutralizing is preferred to nitric or acetic acid because the presence of ammonium chloride will hold in solution many of the third and fourth group elements that might otherwise be precipitated with the lead molybdate; besides, chloride salts are more highly ionized than the acetates and hence are stronger electrolytes and tend to prevent formation of colloids. Add 5 to 10 grams of sodium or ammonium acetate to destroy any free mineral acid. The use of hydrochloric acid and the acetate causes the lead molybdate to precipitate in a granular form, to settle rapidly, and to be easily filtered and washed. Weiser[a] recommends the addition of 8 drops of nitric acid before precipitating the molybdenum.

PRECIPITATION.

The precipitation is best made by titrating the hot molybdenum solution with a lead acetate solution (about 18 grams of crystallized lead acetate per liter) until a test drop gives no color change with a

[a] Weiser, H. B., The physical character of precipitated lead molybdate and its importance in the estimation of molybdenum and lead; Jour. Phys. Chem., vol. 20, 1916, pp. 640–62.

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drop of tannic acid solution. Add about 2 c. c. excess lead acetate, 2 or 3 c. c. of acetic acid, and replace the beaker on the hot-plate, keeping the contents just below the boiling point for about 15 or 20 minutes or until the precipitated lead molybdate has crystallized and settled. Filter hot and wash well with hot water. If any colloids run through the paper the washing should be stopped in order to prevent further loss from colloidal lead molybdate running through the paper. If the precipitate is bulky, wash with a 2 per cent solution of sodium or ammonium acetate in order to decrease the possibility of colloidal lead molybdate forming. Weiser[a] suggests that the precipitate be washed twice by decantation with a 2 per cent solution of ammonium nitrate and then be transferred to the filter paper and washed with hot water. The precipitated lead molybdate will be very pure.

The washed filter is placed in a fire-clay annealing cup and ignited at a dull red[b] heat in a muffle. The filter need not be previously dried. After cooling, the precipitate is brushed out of the annealing cup onto the balance pan and weighed. The weight of the lead molybdate times 0.2615 gives the weight of the molybdenum.

EFFECT OF SULPHURIC ACID.

In order to determine the effect of sulphuric acid on the precipitation of molybdenum by lead acetate, the molybdenum was determined in samples taken from a solution of ammonium molybdate when no sulphuric acid was present, and in the presence of 15 c. c. of concentrated sulphuric acid in samples containing amounts of molybdenum equal to those of the first samples. The concentration of the solutions and the procedure were the same as outlined in the detailed gravimetric method.

Fifteen c. c. of sulphuric acid was used because that volume represents approximately 27.60 grams of acid, a greater weight than that of the sulphates that would be present in a sample taken for analysis, even after fuming with 10 c. c. of acid.

The following table shows the results, which indicate that sulphuric acid does not interfere with the precipitation of molybdenum by lead acetate if precautions are taken as described in the details of the gravimetric method, especially as given under "Precipitation" (p. 21). As the solution containing molybdenum is titrated with a lead acetate solution and only 2 c. c. excess is added, the amount of lead sulphate that might form would be readily soluble in the hot acetate solution.

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[a] Weiser, H. B., place cited.

[b] Scott, W. W., Standard methods of chemical analysis; 2d ed., 1917, p. 278.

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TABLE 1.—*Results of precipitation of $PbMoO_4$ with and without sulphuric acid, first series of tests.*

Sample No.	Mo present in sample.	Mo by gravimetric method.		Mo by volumetric method (titration with $KMnO_4$).
		Without H_2SO_4.	In presence of 15 c. c. of concentrated H_2SO_4.	
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
1	6.26	6.26	6.35	6.24
2	6.26	6.27	6.36	6.24
3	6.31	6.31	6.41	6.30
4	6.31	6.31	6.38	6.30

The column of volumetric determinations is added to the table to serve as a check on the gravimetric determinations. The same standard ammonium molybdate solution was used, acidified with sulphuric acid, and then passed through the Jones reductor; the acidity of solution and the procedure were the same as given under the description of the volumetric method.

As a further test two 1-gram and two 0.25-gram samples of a high-grade molybdenite ore were weighed. The 1-gram samples were decomposed with aqua regia and the molybdenum precipitated with lead acetate. The 0.25-gram samples were decomposed with aqua regia and one was fumed with 5 c. c. of concentrated sulphuric acid and the molybdenum precipitated with lead acetate. The results, given in Table 2, justify the conclusion that sulphuric acid does not interfere with the precipitation of lead molybdate if this is conducted as given under "Precipitation" (p. 21).

TABLE 2.—*Results of precipitation of $PbMoO_4$ with and without sulphuric acid, second series of tests.*

Sample.		Mo content by aqua regia decomposition—	
No.	Weight.	Without H_2SO_4.	Followed by addition of 5 c. c. of concentrated H_2SO_4 and boiling to fumes.
	Grams.	*Per cent.*	*Per cent.*
1	1.00	46.25	.....
2	1.00	46.51	.....
3	.25	46.00	.....
4	.25	.....	46.29
Average.	.....	46.25	46.29

No sample ever taken for analysis and decomposed by aqua regia would contain as much sulphates as is produced by 5 c. c. of concentrated sulphuric acid, consequently the amount of lead sulphate

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formed by the small excess of lead acetate (2 c. c.) added to the molybdenum solution when titrating would be rendered soluble in the acetates present. If lead sulphate should be carried down mechanically with the lead molybdate this would, under the vigorous boiling after precipitation, be rendered soluble during the change in form of the bulky lead molybdate to the granular form.

EFFECT OF LIME.

In order to test the effect of lime on the gravimetric method two samples representing 6.31 per cent molybdenum on a 1-gram basis were prepared. To each was added 3 grams of precipitated calcium carbonate just acidified with hydrochloric acid. The molybdenum was then determined in the samples by the procedure given for the gravimetric method. The results, presented in Table 3, show that a large excess of lime will slightly lower the percentage of molybdenum obtained:

TABLE 3.—*Results of precipitation of $PbMoO_4$ in the presence of lime.*

Sample No.	$CaCO_3$ added.	Mo present.	Mo determined.
	Grams.	*Per cent.*	*Per cent.*
1	3.00	6.31	6.09
2	3.00	6.31	6.10

However, as the 3 grams of precipitated calcium carbonate present in these tests lowered the percentage of molybdenum only 0.21, probably the small proportion of lime present in the ordinary run of molybdenum ore does not cause any appreciable difference.

If the ore should be high in lime the molybdenum can be determined by the volumetric ($KMnO_4$) method, or the lime can be removed from the alkaline solution by means of sodium carbonate before precipitating the lead molybdate. Molybdenum remains in solution. Two precipitations should be made, washing the precipitate well each time.

As calcium molybdate is partly precipitated from a solution slightly acidified with acetic acid only when the solution is boiled vigorously for a prolonged period, it is essential that the directions given under "Precipitation" (p. 21) be followed closely.

PURITY OF THE PRECIPITATED LEAD MOLYBDATE.

In order to test the purity of the precipitated lead molybdate that was obtained by the gravimetric method of determination the ignited lead molybdate was weighed, dissolved, and the molybdenum redetermined by reduction in the Jones reductor and titration with potassium permanganate. Table 4 shows the results obtained:

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TABLE 4.—*Results of tests of purity of precipitated $PbMoO_4$.*

Sample No.	Mo content by—		
	Volumetric method ($KmnO_4$).	Gravimetric method ($PbMoO_4$).	$PbMoO_4$, dissolved, titrated with $KmnO_4$.
	Per cent.	*Per cent.*	*Per cent.*
1	5.580	5.550	5.510
2	1.900	2.000	1.960
3	8.530	8.390	8.310
4	6.580	6.560	6.380
5	6.740	6.910	6.690
6	5.520	5.620	5.440
7	.941	.875	.890
8	.203	.208	.200
9	.425	.439	.440
10	.154	.133	.138

The ignited lead molybdate dissolved entirely in hydrochloric acid, thus showing that the precipitate was not contaminated with silica or insoluble material. If vanadium is suspected to be present in the ore, the solution of dissolved lead molybdate can be tested for vanadium by means of hydrogen peroxide. The solution will become reddish brown if any vanadium is present, from the formation of pervanadic acid (HVO_4). This is a very delicate reaction.

Vanadium is precipitated from solution as lead vanadate in precisely the same manner as lead molybdate. The lead vanadate, however, is not weighed, but the vanadium is calculated as in the determination for molybdenum, because the composition of the precipitated lead vanadate is not always definite. The determination of vanadium and molybdenum when occurring together is described elsewhere in this paper under "Separation of Molybdenum from Vanadium" (p. 29).

COMPARISON OF RESULTS BY VOLUMETRIC (POTASSIUM PERMANGANATE) AND GRAVIMETRIC (LEAD MOLYBDATE) METHODS.

ACID DECOMPOSITION.

A series of determinations were made with duplicate samples of a molybdenum solution in order to compare the results of the volumetric and gravimetric methods.

The volumetric method was used for solutions obtained by decomposition of molybdenite ores and flotation products with aqua regia, followed by the addition of sulphuric acid and boiling to fumes. The solutions were cooled, diluted, made ammoniacal, and filtered to remove silica, iron, and alumina. The filtered solutions were acidified with sulphuric acid and passed through a Jones reductor, then titrated with potassium permanganate solution.

The gravimetric ($PbMoO_4$) method was used for solutions obtained by the decomposition with aqua regia of duplicate samples, as for the

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volumetric method. The solutions were cooled, made ammoniacal, and filtered to remove silica, iron, and alumina, then acidified and the molybdenum precipitated as $PbMoO_4$.

Table 5 shows the results obtained:

TABLE 5.—*Comparison of gravimetric ($PbMoO_4$) and volumetric ($KMnO_4$) results, using acid decomposition for both methods.*

Sample No.	Mo content by—		Sample No.	Mo content by—	
	Gravimetric method.	Volumetric method.		Gravimetric method.	Volumetric method.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
1	0.060	0.063	9	0.439	0.425
2	.080	.077	10	5.700	5.780
3	.069	.074	11	5.550	5.580
4	.071	.068	12	8.390	8.530
5	.086	.095	13	2.000	1.900
6	.092	.102	14	6.560	6.480
7	.112	.139	15	.203	.208
8	.100	.114			

On low-grade material, such as the first eight samples given in Table 5, the addition of lead acetate does not produce any perceptible precipitate, though a faint cloudiness may frequently occur. Neither does the tannic acid, outside indicator, show any change in color. After boiling the solution, however, for at least 15 minutes, a precipitate is formed which on swirling the solution with a glass rod will collect on the bottom at the center of the beaker. If, after the solution has been boiled for an hour and then permitted to stand over night, no precipitate is formed, it can be assumed that no molybdenum is present, otherwise, erroneous conclusions are made that none is present or a "trace".

One of the best ways for testing the accuracy of chemical analyses of products obtained in a concentrating mill treating molybdenum ores, is to total the molybdenum content of all the products made in any ore experiment, then calculate whether this footing corresponds with the content in the feed sample. In several series of analyses of flotation products obtained from molybdenite ores, the average deviation for footing the molybdenum content was less than 2 per cent, which vindicates the accuracy of the methods defined in this paper.

ACID DECOMPOSITION AND FUSION WITH SODIUM PEROXIDE.

In order to obtain a comparison of the methods of decomposition a series of tests was made of duplicate samples of molybdenite ores and flotation products. One set was decomposed by aqua regia and the molybdenum then determined by the gravimetric ($PbMoO_4$) method. The other set was decomposed by fusion with sodium peroxide and the molybdenum determined by the volumetric ($KMnO_4$) method. The results are given in Table 6.

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TABLE 6.—*Comparison of gravimetric ($PbMoO_4$) with volumetric ($KMnO_4$) results, using different methods of decomposition.*

Sample No.	Mo content from decomposition by—	
	Aqua regia and determination of Mo by gravimetric ($PbMoO_4$) method.	Na_2O_2 fusion and determination of Mo by volumetric ($KMnO_4$) method.
	Per cent.	*Per cent.*
1	9.25	9.32
2	1.74	1.79
3	.88	.89
4	.32	.45
5	.10	.14
6	.07	.09
7	.06	.08

COMPARISON OF VOLUMETRIC (LEAD ACETATE) AND GRAVIMETRIC (LEAD MOLYBDATE) METHODS, USING FUSION METHODS OF DECOMPOSITION.

As the titration of a dissolved molybdenum salt with lead acetate agreed closely with the gravimetric determination as lead molybdate for pure chemical solutions, these two methods were tried on low-grade ores that had been fused with sodium peroxide. When such a fusion is leached, practically all the silica and alumina will be found in the filtered liquid, besides other bases soluble in excess alkali. Several ores containing less than 1 per cent molybdenum sulphide were tested by titrating with a standard lead acetate solution, 1 c. c. of which was equivalent to 0.00072 gram, or 0.072 per cent Mo on the basis of a 1-gram sample taken for an analysis. The results were erratic and uncertain. Precipitating the molybdenum from the titrated solution and weighing as lead molybdate also gave variable results because, with lead acetate present in the ammonium acetate and acetic acid solution, much aluminum and silica is carried down with the lead molybdate. However, the gravimetric method described in this paper works well for molybdenum solutions that are free from these elements, as when ore is decomposed by acid.

Some of the difficulties given in standard textbooks regarding the titration of a low-grade lead ore with standard ammonium molybdate solution, which is the reverse of the procedure for titrating a low-grade molybdenum ore with a standard lead acetate solution, using an outside indicator of tannic acid, are as follows:

1. The very low percentage of lead (or molybdenum) is difficult to determine on account of the slowness of the reaction.

2. The large amount of dissolved salts that is necessary in the analysis hinders the separation of lead as molybdate and obscures the end point obtained with tannic acid.

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An excess of ammonium salts and ammonium acetate must be avoided, because if such excess is present the results obtained will be too high.

4. Iron, if present, gives a color with tannic acid.

5. Calcium, barium, and several other bases, form more or less insoluble molybdates that interfere with the results.

6. The method is not accurate.

REMOVAL OF INTERFERING ELEMENTS.

SEPARATION OF TUNGSTEN TRIOXIDE FROM MOLYBDENUM TRIOXIDE.

Tungsten if present interferes with the gravimetric determination of molybdenum, as the tungsten is also precipitated by lead acetate, but it may be removed from the ignited, weighed lead molybdate by treating with hydrochloric acid as described by Crookes.[a] He says:

> The HCl solution of the ignited lead salts, to which a few drops of HNO_3 have been added, is evaporated, preferably over the water-bath, until nearly pasty, when the WO_3 filtered off. The weak acid precipitates any WO_3 still unseparated by the evaporation, and is yet strong enough to hold the molybdenum in solution.

Sulphuric acid has also been used. Regarding this method, Crookes[b] makes the following comment:

> Max J. Ruegenberg and Edgar F. Smith[c] effect the separation of tungsten from molybdenum as follows: Their process is based on a statement that tungstic acid is insoluble in concentrated or dilute sulphuric acid, hot or cold, whereas molybdenum trioxide is very easily and rapidly dissolved. Upon trial, it was found that sulphuric acid of specific gravity 1.378 dissolved molybdenum trioxide very readily, and apparently did not affect the tungsten trioxide. Acid of this concentration was therefore used with the following mixture of the two oxides: 0.7355 gram of tungsten trioxide and 0.0185 gram of molybdenum trioxide were digested for a few minutes with 25 c. c. of warm sulphuric acid. The insoluble portion was filtered out, and washed with water containing sulphuric acid. After drying, it was ignited and weighed. It equaled 0.7350 gram.

The other trials, conducted in precisely the same manner, were as follows:

	2	3	4	5	6
	Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*
Tungsten trioxide taken..	1.0638	0.0871	0.3588	0.8868	0.5996
Molybdenum trioxide taken.....	2.2712	.6871	1.1836	1.1986	1.0770
Tungsten trioxide found..	1.0630	.0870	.3587	.8866	.5996

The filtrate containing the dissolved molybdic acid showed no tungstic acid upon examination.

These results indicate that where the two oxides are present together this mode of separation is of value and merits consideration.

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[a] Crookes, William, Select methods in chemical analysis; 4th ed., 1905, p. 196.

[b] Crookes, William, Work cited, pp. 196–197.

[c] Ruegenberg, M. J., and Smith, E. F., The separation of tungsten trioxide from molybdenum trioxide Chemical News, vol. 83, 1901, p. 5: Jour. Am. Chem. Soc., vol. 22, p. 772.

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SEPARATION OF MOLYBDENUM FROM VANADIUM.

If vanadium is present in the ore it can be removed as given under "Interfering Elements" (p. 10), or be precipitated by lead acetate along with the molybdenum as lead vanadate. The ignited and weighed precipitate of lead molybdate and lead vanadate should be dissolved in HNO_3, taken to fumes with H_2SO_4 to remove lead, and the vanadium determined according to the method of Moore and Kithil.[a]

SEPARATION OF IRON.

The following method for the determination of molybdenum in ferromolybdenum by precipitation as $PbMoO_4$ is an improvement on the original method described by Strebinger.[b]

In this process 0.5 to 1.0 gram of finely pulverized ferromolybdenum is fused in an iron crucible with sodium peroxide. The fusion is leached with water and the solution made up to 500 c. c. and filtered. A sample of 100 c. c. is taken and any iron present is removed by adding nitric acid and ammonia. The clear solution is acidified with 5 c. c. excess hydrochloric acid. About 7 grams of sodium or ammonium acetate is added, the solution diluted to about 300 c. c., heated on a hot plate to about 80° C., and the molybdenum precipitated by titrating this hot solution with a solution of lead acetate (about 18 grams per liter), tannic acid being used as an indicator. To this 2 to 3 c. c. excess of lead acetate solution is added, and 2 or 3 c. c. of acetic acid; then the beaker is replaced on the hot plate for 15 or 20 minutes to allow the lead molybdate to crystallize and settle. The solution is filtered hot and washed well, with the precautions as explained under "Precipitation" (p. 21). The filter is ignited at a dull red heat, then cooled. The ignited lead molybdate is brushed out of the annealing cup onto the balance pan and weighed. The weight of lead molybdate times 0.2615 gives the weight of the molybdenum.

This modification makes the method much shorter, because it eliminates two periods of 6 and 12 hours, respectively, that must otherwise be allowed for the settling of the precipitated lead molybdate.

SEPARATION OF OTHER ELEMENTS.

The separation of molybdenum from the alkalies, alkaline earths, metals of the ammonium sulphide group, metals of Group II, etc., is described in detail by Treadwell and Hall.[c]

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[a] Moore, Richard B., and Kithil, Karl L., A preliminary report on uranium, radium, and vanadium, Bull. 70, Bureau of Mines, 1916, pp. 90–91. Scott, W. W., Standard methods of chemical analysis, 2d ed., 1917, p. 282.

[b] Strebinger, Robert, Ein Beitrag zur quentitativen Bestimmung des Molybdäns, als Bleimolybdat: Chem. Zentralb., Jahrg. 89, 1918, p. 378.

[c] Treadwell, F. P., and Hall, W. T., Analytical Chemistry, vol. 2, 3d ed., 1912, pp. 286–289.

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CONCLUSIONS AS TO GRAVIMETRIC METHOD.

1. This method is applicable to high-grade as well as low-grade material.

2. The molybdenum is readily converted to ammonium molybdate and obtained in a solution practically free from silica, iron, and alumina, and also from lead, if the sample has been fumed with sulphuric acid.

3. Sulphates do not interfere with the determination.

4. A very short time is required for precipitation of the molybdenum as lead molybdate.

5. The precipitate is easily filtered and washed.

6. No special precaution is necessary.

7. No special manipulative skill is required.

8. No special equipment is necessary and no standard solutions are needed.

9. The method is not as rapid as titration with potassium permanganate, following fusion with sodium peroxide and reduction in a Jones reductor.

10. The method is not practicable when fusion is necessary to decompose the ore.[a]

[a] Horton, F. W., Molybdenum: Its ores and their concentration, Bull. 111, Bureau of Mines, 1916, p. 41.

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SELECTED BIBLIOGRAPHY ON DETERMINATION OF MOLYBDENUM.

ANDERSON, C. See Westling, W.

ANDREWS, L. W. Titrations with potassium iodate. Jour. Am. Chem. Soc., vol. 25, 1903, p. 756.

AUCHY, GEORGE. A note on the determination of molybdenum in steel. Jour. Am. Chem. Soc., vol. 24, 1902, p. 273.

———. Caustic soda method of determining molybdenum in steel. Jour. Am. Chem. Soc., vol. 27, 1905, p. 1240; Iron Age, vol. 70, Nov. 20, 1902, p. 4.

BINDER, O. See Hoepfner, W.

BLAIR, A. A. Chemical analysis of iron and steel. 1918. 318 pp.

BREARLEY, HARRY. A bibliography of steel works analysis: Part 2, Tungsten and molybdenum Chem. News, vol. 81, Feb. 2, 1900, pp. 49, 64, 76.

BROWNING, P. E. Introduction to rarer elements. 1917. 158 pp.

COLLETT, E., and ECKHARDT, M. Estimation of molybdenum in molybdenite. Chem. Ztg., Jahrg. 33, 1909, pp. 968–969; Chem. Soc. Abs., vol. 96, 1909, p. 941.

CROOKES, W. Select methods in chemical analysis. 1905. 718 pp.

CRUSER, F. V. D. and MILLER, E. H. Determination of molybdenum in steel and steel making alloys. Jour. Am. Chem. Soc., vol. 26, 1904, p. 675.

DANESI, L. See Mauro, F.

DARROCH, J., and MEIKLEJOHN, C. D. A rapid method of determining molybdenum. Eng. and Min. Jour., vol. 82, 1906, p. 818.

DAVIS, R. S. Notes on technical analysis—Analysis of wulfenite ores. Met. and Chem. Eng., vol. 9, 1911, p. 458.

ECKHARDT, M. See Collett, E.

EDGAR, GRAHAM. The determination of vanadic and molydbic acids in the presence of one another. Am. Jour. Sci., ser. 4, vol. 25, 1908, pp. 332–334.

EPPERSON, C. S. Determination of molybdenum in wulfenite ores. Chem. Analyst, vol. 43, 1918, p. 9; Eng. and Min. Jour., vol. 107, 1919, p. 242.

EVANS, J. C. Determination of molybdenum in wulfenite. West. Chemist and Metallurgist, vol. 3, 1907, pp. 218–219.

FISCHER, A., and WEISE, J. Über die elektro-analytische Bestimmung des Molybdäns. Ztschr. anal. Chem., Jahrg. 51, 1912, pp. 537–550.

FRANK, HENRY. See Miller, E. H.

GOOCH, F. A. Methods of chemical analysis. 1912. 536 pp.

GOOCH, F. A., and FAIRBANKS, CHARLOTTE. The iodometric estimation of molybdic acid. Am. Jour. Sci., ser. 4, vol. 2, 1896, p. 156.

GOOCH, F. A., and PULLMAN, O. S., jr. The estimation of molybdic acid reduced by hydriodic acid. Am. Jour. Sci., ser. 4, vol. 12, 1901, p. 449.

HOEPFNER, W., and BINDER, O. Determination of molybdenum in the presence of copper. Chem. Ztg., Jahrg. 42, 1918, pp. 301–302; Jour. Soc. Chem. Ind., vol. 37, p. 488A. (Advises electrolytic separation.)

HORTON, F. W. Molybdenum; its ores and their concentration. Bull. 111, Bureau of Mines, 1916, pp. 41–44.

JAMISON, G. S. On the determination of molybdenum by potassium iodate. Jour. Am. Chem. Soc., vol. 39, 1917, pp. 246–249.

JOHNSON, O. C. See Prescott, A. B.

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JOHNSON, C. M. Rapid methods for the chemical analysis of special steels, steel-making alloys, and graphite. 1914. pp. 115–133.

KNECHT, E. and STACK, F. W. Volumetric estimation of molybdenum. Analyst, vol. 36, 1911, pp. 98–100.

LORD, N. W., and DEMOREST, D. J. Metallurgical analysis. 1916. 342 pp.

LOW, A. H. Technical methods of ore analysis. 1913. 362 pp.

MAREE, H. C. Molybdenum content of ores and concentrates. Canadian Engineer, vol. 34, Jan. 3, 1918, p. 14; Abstract in Eng. and Min. Jour., vol. 105, 1918, p. 836.

——— Volumetric method for the determination of molybdenum in ferromolybdenum. Canadian Chem. Jour., vol. 2, 1918, p. 132; abstract in Chem. Abs., vol. 12, 1918, p. 1446.

MAURO, F. and DANESI, L. Ueber eine neue Methode zur volumetric Bestimmung des Molybdäns. Ztschr. anal. Chem., Jahrg. 201, 1881, p. 507.

MEIKLEJOHN, C. D. See Darroch, J.

MILLER, E. H. See Cruser, F. V. D.

MILLER, E. H. and FRANK, HENRY. On the reduction of molybdenum by zinc and the ratio of bismuth to molybdenum in bismuth ammonium molybdate. Jour. Am. Chem. Soc., vol. 25, 1903, p. 919.

MARBAKER, E. E. The separation of tungsten from molybdenum. Jour. Am. Chem. Soc., vol. 37, 1915, pp. 86–95.

MOIR, JAMES. Some new methods of testing for molybdenum. Jour. Chem. Met. Min. Soc. South Africa, vol. 16, 1916, pp. 191–192.

OHLY, J. Molybdenite; its determination, detection, and uses. Min. Reporter, vol. 50, 1904, p. 10.

PRESCOTT, A. B. and JOHNSON, O. C. Qualitative chemical analysis. 5th ed., 1903, p. 96.

PULLMAN, O. S. See Gooch, F. A.

RANDALL, D. L. Behavior of molybdic acid in the zinc reductor. Am. Jour. Sci., ser. 4, vol. 24, 1907, pp. 313–316.

RATHER, J. B. Molybdic acid. Jour. Assoc. Official Agr. Chem., vol. 1, 1915, pp. 317–329; vol. 2, 1916, p. 39.

ROSE, HEINRICH. Handbuch der analytische Chemie. Bd. 2. 1867. p. 358.

RUEGENBERG, M. J. and SMITH, E. F. Separation of molybdenum trioxide from tungsten trioxide. Jour. Am. Chem. Soc., vol. 22, 1900, p. 772; Chemical News, vol. 83, 1901, p. 5.

SCOTT, W. W. Standard methods of chemical analysis. 2d ed., 1917, pp. 275–282.

SMITH, E. F. See Ruegenberg, M. J, see Wherry, E. T.

STACK, W. See Knecht, E.

TRAUTMANN, W. Estimation of molybdenum in calcium molybdate. Ztschr. angew. Chem., Jahrg. 23, 1910, p. 1981; Chem. Soc. Abs., vol. 98, p. 1114.

———. Analysis of molybdenite. Chem. Ztg., Jahrg. 33, 1909, pp. 1106–1107.

TREADWELL, F. P. and HALL, W. T. Analytical chemistry. Vol. 2, 3d ed., 1912, pp. 284–666.

WEISER, H. B. The physical character of precipitated lead molybdate and its importance in the estimation of molybdenum and lead. Jour. Phys. Chem., vol. 20, 1916, pp. 640–662.

WEISE, J. See Fischer, A.

WESTLING, W., and ANDERSON, C. Analysis of molybdenum ores. Min. and Sci. Press, vol. 113, 1916, pp. 917–918.

WHERRY, E. T., and SMITH, E. F. Use of a rotating anode in the electrolytic precipitation of uranium and molybdenum. Jour. Am. Chem. Soc., vol. 29, 1907, p. 806.

WOLF, H. J. Tests for molybdenum. Colorado School of Mines Mag., vol. 8, 1918, p. 73; abstract in Min. and Sci. Press, vol. 116, 1918, p. 624.

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